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Chemiluminescence

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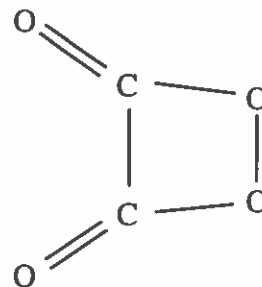
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1,2-dioxetanedione driven chemiluminescence

Overview

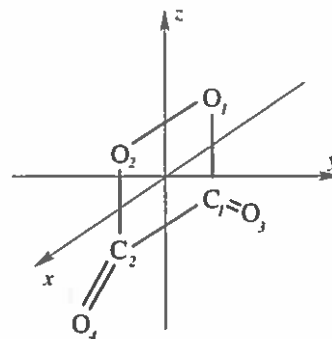
1,2-dioxetanedione is a planar molecule with the conventional chemical structure shown at right. The molecule is essentially an unstable dimer of two CO_2 molecules.



The process of interest is the dissociation of the dimer into two CO_2 molecules, for this produces a CO_2 molecule in an electronically excited state. In the *firefly* or the *glowstick*, the excitation energy of the excited CO_2 molecule is transferred to a dye molecule which subsequently fluoresces in the visible.

Geometry

To describe the geometry of the dissociation, let us embed the molecule in a Cartesian coordinate system in which all the atoms lie in the x, z -plane. Subscripts have been added to distinguish the different atoms.



The dissociation will be modelled by starting the atoms at locations deduced from simple bond length estimates and then moving all the atoms with $x > 0$ a distance Δ along the x -axis and all atoms with $x < 0$ a distance $-\Delta$ along the x -axis, with $\Delta = 0.0\text{ nm}, 0.2\text{ nm}, \dots, 2.0\text{ nm}$. In total, 11 different *EHT* calculations were made. In the diagram at right, the numbers represent the positions in the x, z -plane of the atoms where state calculations were performed. The initial $O_1 - O_2$, $O_1 - C_1$ and $C_1 - O_3$ bond lengths were 1.09 nm .

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The *real* dissociation path deviates from this calculated path because the calculated path does not locate the true minimum energy configuration of the ground state of the

system. It is qualitatively correct, however, and that is all that is required to identify the qualitative result that one of the CO_2 molecules ends up in an electronically excited state.

Molecular Symmetry

There are four symmetry transformations that leave the molecule invariant. Let E denote the identity transformation

C_2 denote the rotation by angle π about the z -axis

σ denote the reflection in the z, y -plane

σ' denote the reflection in the z, x -plane

All these transformations leave the molecule invariant. The set of transformations $\{E, C_2, \sigma, \sigma'\}$ forms a group. The Schönflies symbol for this group is C_{2v} and the character table is

C_{2v}	E	C_2	σ	σ'
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

This symmetry describes the molecule at all Δ . That is, the dissociation path was chosen to not alter the symmetry of the molecule.

The orbitals deduced from EHT

There are 6 atoms in the molecule. Each atom will contribute four Slater type orbitals,

$$2S, 2P_x, 2P_y, 2P_z$$

So there are 24 orbitals. There are 32 valence electrons, so the *aufbau* principle says that the 16 lowest energy orbitals will be filled in the electronic ground state.

The *EHT ansatz* is that the orbitals and energies are determined by solving something like

$$\hat{H} \psi = E \hat{S} \psi$$

with \hat{H} and \hat{S} symmetric, 24×24 matrices. The eigenvalues of this system are the same as the eigenvalues of the matrix $\hat{S}^{-1} \hat{H}$. But $\hat{S}^{-1} \hat{H}$ is not symmetric so the eigenvectors discovered this way are not orthogonal. This can be worked around in various ways, but – since the *symmetry* of the orbitals is important – we can simply start by constructing a symmetry adapted basis set.

Orbital Symmetries

There are 6 atoms in the molecule. Here is how the 24 Slater type orbitals are transformed by the transformations E, C_2, σ and σ' of C_{2v} :

E	C_2	σ	σ'
$2S_{O_1}$	$2S_{O_2}$	$2S_{O_2}$	$2S_{O_1}$
$2S_{O_2}$	$2S_{O_1}$	$2S_{O_1}$	$2S_{O_2}$
$2S_{O_3}$	$2S_{O_4}$	$2S_{O_4}$	$2S_{O_3}$
$2S_{O_4}$	$2S_{O_3}$	$2S_{O_3}$	$2S_{O_4}$
$2S_{C_1}$	$2S_{C_2}$	$2S_{C_2}$	$2S_{C_1}$
$2S_{C_2}$	$2S_{C_1}$	$2S_{C_1}$	$2S_{C_2}$
$2P_{x,O_1}$	$-2P_{x,O_2}$	$-2P_{x,O_2}$	$2P_{x,O_1}$
$2P_{x,O_2}$	$-2P_{x,O_1}$	$-2P_{x,O_1}$	$2P_{x,O_2}$
$2P_{x,O_3}$	$-2P_{x,O_4}$	$-2P_{x,O_4}$	$2P_{x,O_3}$
$2P_{x,O_4}$	$-2P_{x,O_3}$	$-2P_{x,O_3}$	$2P_{x,O_4}$
$2P_{x,C_1}$	$-2P_{x,C_2}$	$-2P_{x,C_2}$	$2P_{x,C_1}$
$2P_{x,C_2}$	$-2P_{x,C_1}$	$-2P_{x,C_1}$	$2P_{x,C_2}$
$2P_{y,O_1}$	$-2P_{y,O_2}$	$2P_{y,O_2}$	$-2P_{y,O_1}$
$2P_{y,O_2}$	$-2P_{y,O_1}$	$2P_{y,O_1}$	$-2P_{y,O_2}$
$2P_{y,O_3}$	$-2P_{y,O_4}$	$2P_{y,O_4}$	$-2P_{y,O_3}$
$2P_{y,O_4}$	$-2P_{y,O_3}$	$2P_{y,O_3}$	$-2P_{y,O_4}$
$2P_{y,C_1}$	$-2P_{y,C_2}$	$2P_{y,C_2}$	$-2P_{y,C_1}$
$2P_{y,C_2}$	$-2P_{y,C_1}$	$2P_{y,C_1}$	$-2P_{y,C_2}$
$2P_{z,O_1}$	$2P_{z,O_2}$	$2P_{z,O_2}$	$2P_{z,O_1}$
$2P_{z,O_2}$	$2P_{z,O_1}$	$2P_{z,O_1}$	$2P_{z,O_2}$
$2P_{z,O_3}$	$2P_{z,O_4}$	$2P_{z,O_4}$	$2P_{z,O_3}$
$2P_{z,O_4}$	$2P_{z,O_3}$	$2P_{z,O_3}$	$2P_{z,O_4}$
$2P_{z,C_1}$	$2P_{z,C_2}$	$2P_{z,C_2}$	$2P_{z,C_1}$
$2P_{z,C_2}$	$2P_{z,C_1}$	$2P_{z,C_1}$	$2P_{z,C_2}$

Projecting the original orbitals into a symmetry adapted basis set gives 9 orbitals with a_1 symmetry, 3 orbitals with a_2 symmetry, 3 orbitals with b_1 symmetry, and 9 orbitals with b_2 symmetry:

irreducible representation	ψ
a_1	$2S_{O_1} + 2S_{O_2}$
a_1	$2S_{O_3} + 2S_{O_4}$
a_1	$2S_{C_1} + 2S_{C_2}$
a_1	$2P_{x,O_1} - 2P_{x,O_2}$
a_1	$2P_{x,O_3} - 2P_{x,O_4}$
a_1	$2P_{x,C_1} - 2P_{x,C_2}$
a_1	$2P_{z,O_1} + 2P_{z,O_2}$
a_1	$2P_{z,O_3} + 2P_{z,O_4}$
a_1	$2P_{z,C_1} + 2P_{z,C_2}$
a_2	$2P_{y,O_1} - 2P_{y,O_2}$
a_2	$2P_{y,O_3} - 2P_{y,O_4}$
a_2	$2P_{y,C_1} - 2P_{y,C_2}$
b_1	$2P_{y,O_1} + 2P_{y,O_2}$
b_1	$2P_{y,O_3} + 2P_{y,O_4}$
b_1	$2P_{y,C_1} + 2P_{y,C_2}$
b_2	$2S_{O_1} - 2S_{O_2}$
b_2	$2S_{O_3} - 2S_{O_4}$
b_2	$2S_{C_1} - 2S_{C_2}$
b_2	$2P_{x,O_1} + 2P_{x,O_2}$
b_2	$2P_{x,O_3} + 2P_{x,O_4}$
b_2	$2P_{x,C_1} + 2P_{x,C_2}$
b_2	$2P_{z,O_1} - 2P_{z,O_2}$
b_2	$2P_{z,O_3} - 2P_{z,O_4}$
b_2	$2P_{z,C_1} - 2P_{z,C_2}$

It is easy to construct an orthonormal basis set from these states. In this basis set, \hat{H} and \hat{S} will be block diagonal, the blocks associated with the irreducible representations.

Looking at this list of symmetry adapted orbitals, it is clear that the a_1 symmetry orbitals are *bonding* orbitals between the two CO_2 parts of the molecule, the a_2 symmetry orbitals are *anti-bonding* orbitals within each of the CO_2 parts, the b_1 symmetry orbitals are the *bonding* orbitals corresponding to the a_2 orbitals, and the b_2 symmetry orbitals are the *anti-bonding* orbitals corresponding to the a_1 orbitals.

Orbital Energies

For each of the 11 configurations, the *overlap* integrals were calculated for all 276 pairs of orbitals and the *EHT* \hat{H} and \hat{S} were constructed.

Evaluating the \hat{H} and \hat{S} in the symmetry adapted basis set identifies the four blocks corresponding to the different irreducible representations. The eigenvalues associated with each block were determined by calculating the eigenvalues of the corresponding $\hat{S}^{-1} \hat{H}$ blocks.

The three energies associated with the a_2 irreducible representations are -28.541 eV, -13.618 eV, and -13.618 eV for *all* configurations (consistent with the view that these are *anti-bonding* orbitals in the separate CO_2 molecules) and the three energies associated with the b_1 irreducible representations are -20.377 eV, -11.26 eV, and -11.26 eV for *all* configurations (consistent with the view that these are *bonding* orbitals in the separate CO_2 molecules).

The following four tables give the orbital energies associated with the four irreducible representations as a function of the distortion parameter Δ .

a_1 orbital energies (eV) as a function of Δ (column #1)

0.0	-38.2657	-15.4148	-14.5817	-14.2963	-13.1989	-12.84	-12.8358	12.1444	66.7007
0.2	-37.7946	-15.8602	-14.4931	-14.2021	-13.3426	-12.9655	-12.9585	5.04851	51.0382
0.4	-37.277	-16.616	-14.394	-14.112	-13.458	-13.081	-13.071	-1.80249	44.5087
0.6	-36.732	-17.859	-14.2962	-14.02	-13.549	-13.185	-13.17	-6.79335	41.7094
0.8	-36.177	-19.629	-14.20	-13.955	-13.62	-13.276	-13.257	-9.74617	40.4587
1.0	-35.632	-21.586	-14.12	-13.8907	-13.674	-13.353	-13.329	-11.2878	39.8998
1.2	-35.116	-23.352	-14.054	-13.8361	-13.713	-13.417	-13.390	-12.1026	39.6607
1.4	-34.64	-24.787	-13.99	-13.7905	-13.738	-13.470	-13.439	-12.5713	39.5633
1.6	-34.23	-25.89	-13.9478	-13.753	-13.752	-13.512	-13.479	-12.8647	39.5194
1.8	-33.88	-26.720	-13.9081	-13.757	-13.72	-13.544	-13.510	-13.0606	39.4874
2.0	-33.613	-27.320	-13.8751	-13.756	-13.698	-13.568	-13.535	-13.1979	39.4507

 a_2 orbital energies (eV) as a function of Δ (column #1)

0.0	-11.26	-11.26	-11.26
0.2	-11.26	-11.26	-11.26
0.4	-11.26	-11.26	-11.26
0.6	-11.26	-11.26	-11.26
0.8	-11.26	-11.26	-11.26
1.0	-11.26	-11.26	-11.26
1.2	-11.26	-11.26	-11.26
1.4	-11.26	-11.26	-11.26
1.6	-11.26	-11.26	-11.26
1.8	-11.26	-11.26	-11.26
2.0	-11.26	-11.26	-11.26

 b_1 orbital energies (eV) as a function of Δ (column #1)

0.0	-20.337	-11.26	-11.26
0.2	-20.337	-11.26	-11.26
0.4	-20.337	-11.26	-11.26
0.6	-20.337	-11.26	-11.26
0.8	-20.337	-11.26	-11.26
1.0	-20.337	-11.26	-11.26
1.2	-20.337	-11.26	-11.26
1.4	-20.337	-11.26	-11.26
1.6	-20.337	-11.26	-11.26
1.8	-20.337	-11.26	-11.26
2.0	-20.337	-11.26	-11.26

 b_2 orbital energies (eV) as a function of Δ (column #1)

0.0	-34.9595	-17.1363	-14.04	-13.9652	-13.5398	-13.2506	-13.2454	-10.7231	-6.18174
0.2	-34.1797	-18.7006	-14.0039	-13.8995	-13.6168	-13.3201	-13.2906	-11.0314	-9.16851
0.4	-33.4122	-20.5434	-13.97	-13.8435	-13.6771	-13.3821	-13.3274	-11.7662	-10.0706
0.6	-32.6792	-22.2645	-13.9385	-13.7967	-13.7212	-13.4329	-13.361	-12.3916	-10.2631
0.8	-31.9995	-23.6959	-13.9093	-13.7582	-13.75	-13.4739	-13.3916	-12.7755	-10.3273
1.	-31.3864	-24.8323	-13.8825	-13.7654	-13.727	-13.5066	-13.4194	-13.016	-10.3568
1.2	-30.848	-25.7177	-13.8579	-13.7696	-13.7021	-13.5325	-13.4446	-13.1751	-10.3727
1.4	-30.3864	-26.4016	-13.8357	-13.7651	-13.6824	-13.5528	-13.4672	-13.2855	-10.382
1.6	-29.9995	-26.9272	-13.8158	-13.7544	-13.667	-13.5685	-13.4876	-13.3648	-10.3879
1.8	-29.6817	-27.3298	-13.7981	-13.7401	-13.6551	-13.5807	-13.5058	-13.4234	-10.3917
2.0	-29.4252	-27.637	-13.7824	-13.7241	-13.6459	-13.59	-13.5221	-13.4675	-10.3944

For each Δ , the *aufbau* principle will identify the ground state of the system as the state in which the 16 lowest energy orbitals will be occupied by 32 electrons. Plotting the orbital energies as a function of Δ is confusing because there are so many (24) and because the orbital energies of different irreducible representations can (and do) cross each other. In the following table, the *symmetries* of the orbitals found at each Δ are listed in columns. The order of the listing is such that, as one rises in a column one encounters the orbitals in the order of increasing orbital energy.

Δ	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1
	a_1	a_1	a_1	a_1	a_1	b_2	b_2	b_2	b_2	b_2	b_2
	b_2	b_2	b_2	b_2	b_2	b_1	b_1	b_1	b_1	b_1	b_1
	b_2	b_2	b_1	b_1	b_1	b_1	b_1	b_1	b_1	b_1	b_1
	b_1	b_1	b_1	b_1	b_1	a_2	a_2	a_2	a_2	a_2	a_2
	b_1	b_1	a_2	a_2	a_2	a_2	a_2	a_2	a_2	a_2	a_2
	a_2	a_2	a_2	a_2	a_2	a_2	a_2	a_2	a_2	a_2	a_2
	a_2	a_2	a_2	a_2	a_2	a_1	a_1	a_1	a_1	a_1	a_1
	a_2	a_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2
	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1	b_2	b_2
	a_1	a_1	a_1	a_1	a_1	a_1	a_1	b_2	b_2	a_1	a_1
	a_1	b_2	b_2	b_2	b_2	b_2	b_2	a_1	a_1	a_1	a_1
	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2
	b_2	a_1	a_1	a_1	a_1	a_1	b_2	b_2	b_2	b_2	b_2
	b_2	b_2	b_2	b_2	b_2	b_2	a_1	a_1	a_1	a_1	a_1
	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2	a_1	b_2	b_2
	b_2	b_2	b_2	b_2	b_2	b_2	a_1	a_1	b_2	a_1	a_1
	a_1	a_1	a_1	a_1	a_1	a_1	b_2	b_2	b_2	b_2	b_2
	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1
	a_1	a_1	a_1	a_1	a_1	b_1	b_1	b_1	b_1	b_1	b_1
	b_2	b_2	b_1	b_1	b_1	a_1	a_1	a_1	a_1	a_1	a_1
	b_1	b_1	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2
	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2	b_2
	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1	a_1

In this table, a horizontal line has been drawn above the 16th level. At each Δ , the ground state configuration will consist of all the levels below this line filled and no levels above this line filled.

A rough image of the crossing of the levels as Δ is changed can be generated by passing lines through the symmetry symbols of the orbitals. The lowest energy orbital, for example, does not change with Δ . But the highest occupied orbital (a_2 at $\Delta = 0.0$) moves out of the ground state configuration as Δ passes from 0.2 \rightarrow 0.4! It is replaced as the highest energy occupied orbital by a b_2 symmetry orbital whose energy descends rapidly as Δ rises.

Thus, if we start in the ground state with $\Delta = 0$ and increase Δ *adiabatically*, the state will pass from a ground state configuration into an excited state configuration when Δ passes from 0.2 \rightarrow 0.4.

If we suppose the de-excitation occurs when the molecule has a configuration $\approx \Delta = 2.0$, the energy that will be transferred to the dye will be the energy difference between the a_2 and b_2 orbitals in configuration $\Delta = 2.0$, $-11.26 \text{ eV} + 13.4675 \text{ eV} = 2.21 \text{ eV}$. As a red photon has an energy $\approx 1.65 \text{ eV}$, there is clearly enough energy to excite the dye!

Some additional notes

In commercial software it is always easy to *optimize* the structure, i.e., move around on the Born-Oppenheimer surface to find the structure with a minimum energy. I did not cover in the class the *Feynmann-Hellman* theorem that shows that an essentially classical calculation can be used to determine the force on atoms in any given configuration (and hence it is easy move toward an energy minimum).

The orbital description doesn't tell *which* CO_2 molecule ends up in an excited state. But that is a classical question. Quantum mechanics recognizes the symmetry of the situation: It's possible to have a state in which the probability that either CO_2 molecule is excited is "50-50".

In fact, the description that "a CO_2 molecule is excited" is inaccurate, for it is based on the assumption that the orbital occupation remains constant in the dissociation process. This turns out not to be correct: The *ESR* spectroscopists were able to observe

that the dissociating complex went through a *biradical* configuration. Two separate one-electron jumps doesn't actually occur. Rather, the biradical is formed and it is the rearrangement of the electrons in the biradical that provides the energy for the light emission.